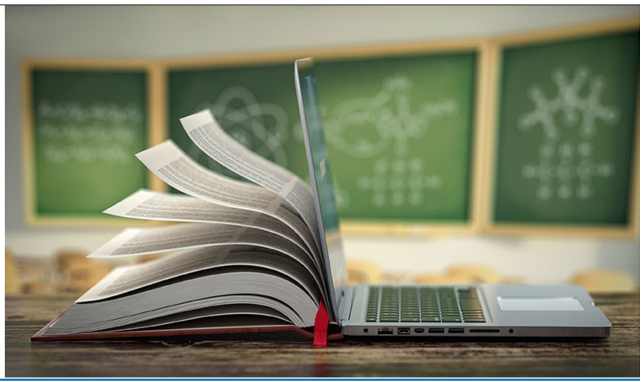
PAPER • OPEN ACCESS

The Melt Heat Treatment and the Structural Changes in ZhS6U and Inconel 718

To cite this article: Dmitry Tarasov *et al* 2021 *J. Phys.: Conf. Ser.* **1888** 012005



The Melt Heat Treatment and the Structural Changes in ZhS6U and Inconel 718

Dmitry Tarasov, Andrey Tyagunov, Oleg Milder

Ural Federal University, Mira 32-R041, Ekaterinburg, Russia, 620002

datarasov@yandex.ru

Abstract. One of the most curious phenomena observed in metal melts is the temperature-induced liquid-liquid structural changes. As a result of the thermal treatment lead to LLT, a more equilibrium and micro-uniform melt consisting of atomic associations is formed. In nickel alloy melts, the changes that have occurred are irreversible and have a significant effect on the formation of the final structure and the mechanical properties of the metal in the solid state after its crystallization. In addition, they are the starting point for the scientific substantiation of new technological modes of smelting and heat treatment of alloys, which further improve their operational properties, as well as reduce metallurgical defects and production waste, and rational use of expensive ligands. All this in general will lead to a significant increase in the performance of melts and metal products. Our work is devoted to the experimental confirmation of the LLT transition in two common nickel-based alloys by a non-invasive electromagnetic method.

1. Introduction

The studied ZhS6U and Inconel 718 alloys are widely applied to manufacturing gas turbine engine parts and devices. The alloys using nickel matrix consist of the main alloying elements Co, Mo, W, Al, Cr, Ti, Nb, Ta, Re, Ru, Fe, B, C, and, also, contain different impurities like S, Si, P and O, N as dissolved gases. The current set of properties of these alloys is achieved by optimizing the content of the main alloying elements in their chemical composition. Further change in the alloyage and implantation of new elements leads to a deterioration in the crystal structure and the alloys service properties [1]. An important reserve for improving the properties of metallic materials is laid in the technology of heat treatment of their melts [2].

To draw up such technologies, it is necessary to carefully account the structural changes of the melts that occur during heating and subsequent cooling. The liquid-liquid transitions in melts are reflected in the behavior of polytherms (temperature (t) induced behavior) of their structurally sensitive properties, such as density, (kinematic) viscosity, electrical resistivity, surface tension, *etc*. Research experience indicates that the noninvasive electromagnetic method of electrical resistivity (ρ) determination is the most structurally sensitive when studying the properties of such complex materials as high-temperature nickel-based alloys in the liquid state [3].

2. Electrical resistivity vs temperature for ZhS6U and Inconel 718

The dependence $\rho=f(t)$ for sequential stages of heating and cooling of melts of the studied alloys (see Fig. 1, I and III) has the form characteristic of most liquid heat-resistant nickel compositions [4]. The heating polytherm manifests a non-monotonic behavior in the electrical resistivity (ρ) values. On the graphs of the heating polytherms, in the region between the identified local extrema, designated as t_{an} and t_k, a zone with an abnormal increase in ρ is fixed. The trajectories of the heating polytherms and the positions of the extrema t_{an} and t_k are described by the common quasi-chemical model of the microheterogeneous state of metallic liquids [4, 5].

This model implies that with an increase in the temperature of the melt, at a certain point in time, phase liquid-liquid transitions (LLT) of the second kind occur, which are a reflection of a significant change in the structure of the melt [4, 6]. Immediately after melting, nonequilibrium atomic microgroups are formed, which after LLT transform into more equilibrium ones, but already possessing different properties of short-range order [7]. The region of the abnormal increase in ρ values, which boundaries are the points t_{an} and t_k, corresponds to the LLT structural changes for this melting alloy.

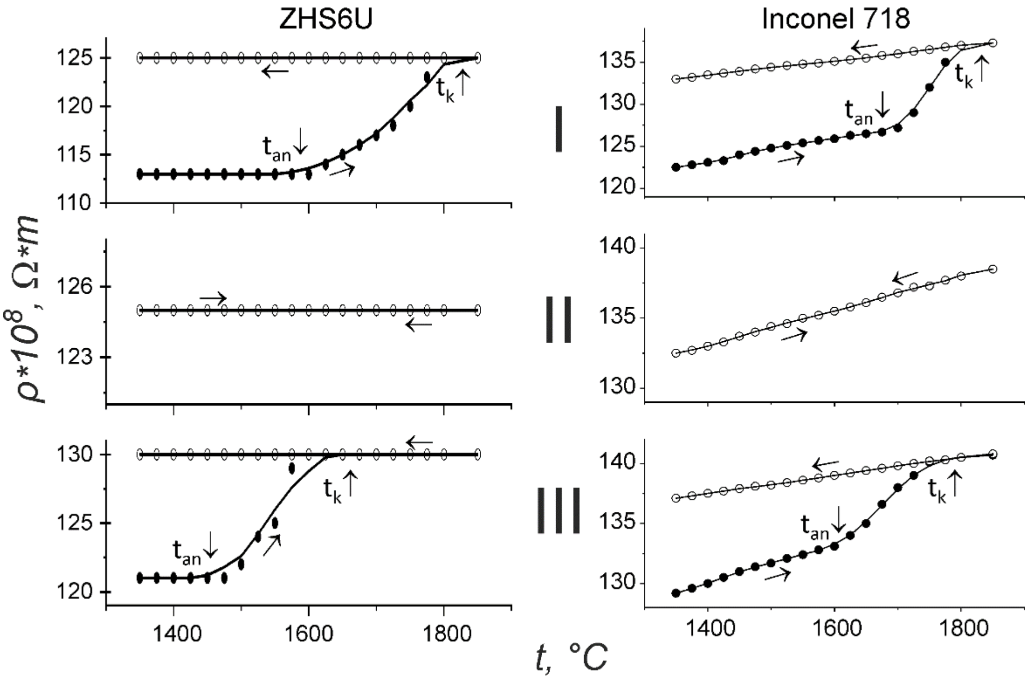


Figure 1. Heating (right arrows) and cooling (left arrows) electrical resistivity polytherms for the liquid ZhS6U (left) and Inconel 718 (right) alloys; roman numerals indicate the experiment mode number.

The observed difference between the forward and the reverse branches of the polytherms indicates the phenomenon of hysteresis, which has been observed by numerous researchers of the physical properties of melts [7, 8]. Before the end of the liquid-liquid transitions and structural changes in melts, the differences in the electrical resistivity (ρ) values between the upper and the lower polytherms branches indirectly indicate the disequilibrium grade of the melt. The specimens of alloys, preheated to temperatures exceeding t_k, exhibit linear cooling polytherms, *i.e.* LLT changes are retained upon cooling in a fairly wide temperature range, and as a result, the melt is in a more equilibrium state before solidification, which has a positive effect on the properties of the solid.

A remarkable property of such structural changes is that once having reached an equilibrium microhomogeneous state, the structure of the melt does not undergo a reverse transition in the future, even upon cooling. The metallic liquid remains stable until the onset of crystallization, which indicates the irreversibility of structural changes that have occurred in the melt [9].

3. Experimental

The nonequilibrium state of the melts depends on the microinhomogeneity of the clusters inherited from the solid structure [2]. It is well known that the major constituents of the Ni-based alloys are the γ nickel matrix and the intermetalide γ′-phase formed predominantly by Ni_3(Al, Ti ...). Thus, it can be argued that in Ni-based alloy melts the basic kind of atomic microgroups are clusters based on Ni_3(Al, Ti ...) [2, 10]. To confirm this fact, the following experiment was carried out. The electrical resistivity (ρ) of the alloys specimens was studied in three different heating-cooling modes (Fig. 1). The temperatures of phase transformations during cooling of the studied compositions were previously determined by the method of differential thermal analysis (DTA) (see Table 1).

Table 1. Temperature of phase transformations occurring during cooling of the studied melting compositions according to the differential thermal analysis data, °C.

Alloy	Liquidus	The onset of carbide phase	Solidus	γ'-solvus
ZhS6U	1325	1310	1225	1190
Inconel 718	1336	1300	1260	1015

In the <u>first</u> mode, the ρ values were measuring during heating up to a temperature around (and slightly higher than) t_k, and until the specimen had cooled to a temperature not lower than **liquidus**.
In the <u>second</u> mode, the same specimens were heated to the same maximum temperature as in the previous mode, however, the cooling was carried out below the **liquidus** temperature down to a temperature of **solidus**, but not lower than the **γ'-solvus**. In this case, the intermetallic γ'-phase has not yet precipitated. Further heating of the specimen to a temperature above t_k do not lead to the polytherm hysteresis, *i.e.* the heating and the cooling polytherms coincide. The electrical resistivity (ρ) values corresponded to the equilibrium state is the upper branch of the polytherm. This means that the solid solution matrix formed upon cooling during new melting does not affect the degree of equilibrium and microinhomogeneity of the melt, and the achievement of the LLT transition is preserved.
In the <u>third</u> mode, the specimen underwent LLT and further crystallization was, again, heated slightly above t_k, just like in the first mode, and then was cooled to room temperature and held for at least a week. Next time it was heated again, the polytherms, again, branched. During the new heating to a temperature above t_k, after the end of the crystal structure formation, the ρ abnormal growth region, as well as, the hysteresis phenomenon, were again observed on the heating polytherm.
During this series of experiments, the temperatures of the critical points of melts gradually decreased, while the electrical resistivity increased. These results show that the main reason for the formation of nonequilibrium microinhomogeneous clusters in Ni-based alloys melts is the excess of intermetalide γ'-phase. Its precipitation in the solid structure upon subsequent heating, again, leads to the phenomenon of hysteresis of the electrical resistivity polytherms, i.e. to the formation of nonequilibrium clusters. To transfer such a melt into a homogeneous microhomogeneous state, a new LLT transition with a significantly reduced temperature is required.
Comparing the results obtained and the data of X-ray diffraction studies [10, 11], it can be argued that when the temperature of the melt exceeds the critical value, the lattice parameter and coordination number decrease. This leads to a weakening of interatomic bonds within the cluster and a decrease in its size and the number of its constituent atoms. The number of clusters with a more uniform distribution of elements increases and the melt passes into a microhomogeneous state.
The carbon content in the melting compositions of the studied alloys, as well as the metallographic studies of solid specimens [12, 13], indicate the presence of MS type carbides in the cast structure [14]. According to the DTA analysis, carbide phases nucleate immediately after the onset of solid solution formation [4]; therefore, their growth occurs simultaneously with the development of the solid solution matrix. This means that carbides are formed from intrinsic clusters with similar stoichiometry of MS.

As is known [15], nitrogen is not completely removed from the melt during crystallization and participates in the formation of parasitic nitride phases. This, for example, is typical for a variety of foundry waste, which are remelted by traditional methods during processing, but this does not lead to complete dissolution of nitride particles in the melt. During crystallization, the solid solution obtained from such a melt does not form strong bonds with the particles of these phases, which ultimately leads to defects in metal products. All this impedes the rational use of foundry production waste [16]. Since the dissociation temperature of the nitride phases particles is often higher than the melting temperature of the alloys themselves, it is obvious that refractory nitride particles inside the melt form a specific cluster with stoichiometry MN. With an increase in the temperature of the melt before the onset of structural changes such as LLT, the process of liberation of nitrogen atoms from such nonequilibrium microgroups becomes possible [17], which significantly reduces its concentration in the melt. This leads to the hardening of the alloy.

4. Discussion

Our assumptions about the existence of separate clusters (Ni_3(Al, Ti ...), MS, and MN) in the melts of the studied alloys coincide with the conclusions of [18].

Researchers of [19] argue that the LLT transition is accompanied by polymorphic transformations, regardless the isomorphism of solid solvent elements; as a result, the melt density slightly changes. In our previous works, information on a certain increase in the density of the heat-resistant Ni-based alloys melts as a result of structural changes was, also, given [2].

The completion of LLT in the melt and the attainment of an equilibrium state is considered to be the stability of the cluster sizes in any arbitrarily chosen phase region [20]. In this case, the physical properties of the melts are stabilized and the extrema on the polytherms disappear.

The crystallization of the melt that underwent structural changes in the liquid state is accompanied by increased supercooling, which significantly affects the solidification mechanism, the formation of a solid structure, and, also, contributes to a more uniform distribution of alloying elements over local microvolumes, a decrease in the defectiveness of the solid metal, and a significant refinement in its properties.

Since the crystallization mechanism of melts of high-temperature nickel alloys differs significantly from the crystallization of any other types of alloys, this allows the use of elevated temperatures during melting for the stable passage of all structural transitions and thus the formation of a favorable crystal structure of the alloy, which is realized in improving the properties of the hard alloy. In industry, the discovered influence of LLT on the formation of the cast structure of alloys is used in the development of new technological modes of melting, including heating the melt to t_k, a certain holding, and cooling. Such techniques are called time-temperature melt treatment (TTMT). The TTMT mode for the alloys of the studied melting compositions should provide heating ZhS6U to 1750 °C and Inconel 718 to 1820 °C. For alloys of the same grades, but of other melting compositions, the modes of heat treatment of the melts should be different.

The application of TTMT techniques to the nickel alloy melts has an excellent effect on the properties and quality of metal products and on the technological operations of their production. The melt underwent LLT forms a crystalline structure with improved plastic and strength properties, including impact strength, tensile strength, phase stability, and corrosion resistance, which leads to an increase in the service life of metal products made from such alloys [21, 22]. Descent in the amount of non-metallic inclusions and gases in the melt, as well as a decrease in the number and size of pores in castings, makes it possible to increase the yield of suitable products and the possibility of using casting waste [15]. To this should be added such measures as supercooling and a decrease in the crystallization interval, which also significantly improves the technological properties of the liquid metal [2, 4].

Thus, we have confirmed the scientific concept of structural changes in multicomponent nickel-based melts from the standpoint of a quasicrystalline model of a microinhomogeneous structure using the example of two conventional nickel alloys. According to this model, immediately after melting, alloys in the liquid phase consist of several simultaneously existing types of atomic clusters (Ni_3(Al, Ti ...), MS, and MN). With a further increase in the melt temperature, a second-order phase transition of the LLT type occurs, which is accompanied by a decrease in the energy of interatomic interaction within the clusters and the release of a certain number of atoms, which form new smaller but also more homogeneous clusters. Such structural changes in melts are irreversible. This contributes to the formation of an improved alloy structure upon cooling and crystallization. This effect is widely used in the smelting of industrial heat-resistant nickel alloys to improve technological properties, correct metallurgical defects, and improve the quality of metal products from these alloys, as well as the use of foundry waste.

References

[1] Kablov E. N. Cast blades of gas turbine engines. Alloys, technology, coatings. Moscow: MISIS. 2001. 632p. (Каблов Е.Н. Литые лопатки газотурбинных двигателей. Сплавы, технология, покрытия. М.: МИСИС. 2001. 632с in Russian).
[2] Baum B.A., Khasin G.A., Tyagunov G.V., et al. Liquid steel. Moscow, Metallurgy, 1984, 208p. (Баум Б.А., Хасин Г.А., Тягунов Г.В. и др. Жидкая сталь. - М., Металлургия, 1984. - 208 с. – in Russian).
[3] Tyagunov A.G., Baryshev E.E., Tyagunov G.V., Mushnikov V.S., Tsepelev V.S. Polytherms of the Physical Properties of Metallic Melts. Steel in Translation, 2017, Vol. 47, No. 4, 250–256.
[4] Tyagunov A.G., Baryshev E.E., Stepanova N.N. The influence of the melt structure on the properties of heat-resistant nickel alloys in the solid state, NISO Ural Branch of RAS, 2010, No.2 (10), 198p. (Тягунов А.Г., Барышев Е.Е., Степанова Н.Н. Влияние структуры расплава на свойства жаропрочных никелевых сплавов в твердом состоянии. НИСО УрО РАН №2 (10), 2010, 198с. – in Russian).
[5] McMillan P. Jumping between liquid states. Nature, 2000, Vol. 403, 151–152.
[6] Rao K.R. Phase transitions in liquids. Curr. Sci, 2001, Vol.80, 1098–1100.
[7] Ying L.W., Chen B.D., Shao. Z. Effects of metalloid content on viscosity of Fe-Si-B-P-C alloy melt. Journal of Non-Crystalline Solids. Vol. 490, 15 June 2018, 31–34.
[8] Sivkov G., Yagodin D., Kofanov S., et al. Physical properties of the liquid Pd-18 at.% Si alloy. J. Non-Crystal. Solids, 2007, Vol.353, 3274–3728.
[9] Xiao C., Qi Z., Xiao L., Zu F.Q. On crystallization behavior and thermal stability of Cu64Zr36 metallic glass by controlling the melt temperature. Journal of Non-Crystalline Solids, 2016, Vol.452, No.9.
[10] Yinab F.S., Suna X.F., Guana H.R., Hua Z.Q. Effect of thermal history on the liquid structure of a cast nickel-base superalloy M963. Journal of Alloys and Compounds. 2004, Vol.364, Iss.1–2, №2, 225–228.
[11] Fredriksson H., Fredriksson E. A model of liquid metals and its relation to the solidification process. Mater.Sci.Eng. A-Struct.Mater, 2005, No.2, 455–459.
[12] Tyagunov A.G., Baryshev E.E., Kostina T.K., Baum B.A., Lesnikov V.P., Semenova I.P. The effect of long-term high-temperature heat treatment at 950°C on the structure and mechanical properties of the zhs6u superalloy. The Physics of Metals and Metallography. 1998. Т. 86. № 1. 65–69.
[13] Mukhtarova K.S., Shakhov R.V., Mukhtarov S.K., Smirnov V.V., Imayev V.M. Microstructure and mechanical properties of the Inconel 718 superalloy manufactured by selective laser melting. Lett. Mater., 2019, 9(4), 480–484.
[14] Kuznetsov V. P., Lesnikov V. P., Popov N. A. Structure and properties of heat-resistant Nickel alloys. Publishing house of the Ural University. 2016. 164p. Кузнецов В.П., Лесников В.П., Попов Н.А. Структура и свойства жаропрочных никелевых сплавов. Издательство Уральского университета. 2016. 164с. in Russian).
[15] Kolotukhin E. V., Avdyukhin S. P., Tyagunov G. V., Larionov V. N. Conditions for the

existence of a nitride phase in a liquid complex-alloyed Nickel alloy. University news. Ferrous metallurgy. 1989. No. 9. 115-120. (Колотухин Э.В., Авдюхин С.П., Тягунов Г.В., Ларионов В.Н. Условия существования нитридой фазы в жидком сложнолегированном никелевом сплаве. Известия вузов. Черная металлургия. 1989. №9. С.115–120. in Russian).

[16] Kablov D. E., Chabina E. B., Sidorov V. V., Min P. G. Investigation of the influence of nitrogen on the structure and properties of single crystals from the foundry heat-resistant alloy ZHS30-VI. Metal science and heat treatment. 2013, No.8, 3–11. (Каблов Д.Е., Чабина Е.Б., Сидоров В.В., Мин П.Г. Исследование влияния азота на структуру и свойства монокристаллов из литейного жаропрочного сплава ЖС30-ВИ. Металловедение и термообработка. 2013. №8. 3–11 in Russian).

[17] Kablov D. E., Sidorov V. V., Gerasimov V. V., Simonov V. N., Min P. G. Research of regularities of nitrogen behavior in obtaining single crystals of heat-resistant Nickel alloy ZHS30VI 77-30569/377117 #4, April 2012 electronic scientific and technical publication Science and education. (Каблов Д.Е., Сидоров В.В., Герасимов В.В., Симонов В.Н., Мин П.Г. Исследования закономерностей поведения азота при получении монокристаллов жаропрочного никелевого сплава ЖС30ВИ 77-30569/377117 #4, апрель 2012 электронное научно-техническое издание Наука и образование http://technomag.edu.ru/doc/377117.html in Russian).

[18] Kaban I., Halm T., Honyer W. Structure of molten copper-germanium alloys. J. Non-Crystal. Solids, 2001, Vol.288, 96–102.

[19] Yarger J.L., Wolf G.H. Polymorphism in Liquids, Science, 2004, V.306, 220–221.

[20] Wang, L.; Bian, X.F.; Liu, J.T. Discontinuous structural phase transition of liquid metal and alloys. Phys. Lett. A, 2004, Vol. 326, 429–435.

[21] Zhenxue S., Shizhong L., Xiaoguang W., Xiao-dai Y., Jia-rong Li. Effect of melting temperature on the microstructure stability of a Ni-based single crystal superalloy. Procedia Engineering, 2015, Vol. 99, 1415–1420.

[22] Haijun S., Haifeng W., Jun Z., Min G., Lin L., Hengzhi F. Influence of Melt Superheating Treatment on Solidification Characteristics and Rupture Life of a Third-Generation Ni-Based Single-Crystal Superalloy. Metallurgical and Materials Transactions B. 2018, Vol.49. № 4. 1537–1546.